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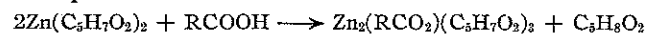
## The Synthesis of a New Series of Zinc Compounds

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In a recent communication<sup>2</sup> we reported the existence of a compound  $\text{Zn}_2(\text{CH}_3\text{CO}_2)(\text{C}_5\text{H}_7\text{O}_2)_3$  formed either by (a) the thermal decomposition of bis(acetylacetonato)-zinc(II) hydrate or (b) heating zinc acetate with acetylacetone. We have now found a superior synthetic route and have applied it to the preparation of a homologous series of compounds having the generalized formula  $\text{Zn}_2(\text{RCO}_2)(\text{C}_5\text{H}_7\text{O}_2)_3$  where  $\text{R} = \text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $\text{C}(\text{CH}_3)=\text{CH}_2$ ,  $\text{C}_6\text{H}_5$ ,  $m\text{-CH}_3\text{C}_6\text{H}_4$ ,  $p\text{-CH}_3\text{C}_6\text{H}_4$ ,  $p\text{-ClC}_6\text{H}_4$ , and  $p\text{-BrC}_6\text{H}_4$  (Table I).

The general route to these compounds is *via* the reaction of anhydrous bis(acetylacetonato)zinc(II) with the calculated amount of an organic acid according to the equation



These white crystalline compounds are only slightly soluble in organic solvents at ambient temperatures. They are, however, soluble in chloroform. The acetate

and methacrylate derivatives are sufficiently soluble in benzene to conduct molecular weight measurements. Polar solvents generally decompose these new compounds.

It is interesting to note that the molecular weights obtained in chloroform are not in agreement with the calculated formula weight. The two derivatives sufficiently soluble in benzene, however, gave molecular weights in agreement with theoretical. The acetate derivative described earlier<sup>2</sup> has been determined at varying concentrations in chloroform. The experimentally found molecular weight does not vary with concentration (7.17 g./l., mol. wt. found 346; 4.51 g./l., mol. wt. found 348; 19.66 g./l., mol. wt. found 386; 6.45 g./l., mol. wt. found 319).

Attempts to prepare similar compounds with other fatty acids higher than propionic acid were unsuccessful.

We assume that the three acetylacetonate groups of these compounds are attached to one zinc atom, leading to a structure with hexacoordinated zinc such as  $\text{Zn}(\text{RCO}_2)[\text{Zn}(\text{C}_5\text{H}_7\text{O}_2)_3]$ . This salt-like structure could account for the poor solubility in organic solvents and the anomalous molecular weights obtained in chloroform. The existence of the  $[\text{Zn}(\text{C}_5\text{H}_7\text{O}_2)_3]^-$  anion, and its low stability in ionizing solvents, has been noted previously.<sup>3</sup>

In this connection sodium tris(acetylacetonato)-zincate(II) was prepared by combining methanol

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(2) G. Rudolph and M. C. Henry, *Inorg. Chem.*, **3**, 1317 (1964).

(3) F. P. Dwyer and A. M. Sargeson, *J. Proc. Roy. Soc. N.S. Wales*, **90**, 29, 141 (1956).

TABLE I

$\text{Zn}_2(\text{RCO}_2) \cdot (\text{C}_6\text{H}_7\text{O}_2)_2$ , R =	Yield, %	M.p., °C.	Mol. wt.			% C		% H	
			Calcd.	Found <sup>a</sup> in		Calcd.	Found	Calcd.	Found
				$\text{C}_6\text{H}_6$	$\text{CHCl}_3$				
$\text{CH}_3$	78	198–200	487.14	<i>b</i>	319	41.92	42.31	4.97	5.06
$\text{CH}_2\text{CH}_2$	67	159–160	501.17	528	328	43.14	43.95	5.23	5.23
$\text{CH}_2=\text{C}(\text{CH}_3)$	55	193–194	513.18	498	446	44.47	44.03	5.11	4.99
$\text{C}_6\text{H}_5$	88	243–245 dec.	549.21	<i>b</i>	340	48.11	49.12	4.77	4.79
<i>m</i> - $\text{CH}_3\text{C}_6\text{H}_4$	72	219–220	563.24	<i>b</i>	422	49.05	50.94	5.01	4.95
<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4$	83	244 dec.	563.24	<i>b</i>	397	49.05	50.78	5.01	4.87
<i>p</i> - $\text{ClC}_6\text{H}_4$	80	257 dec.	583.66	<i>b</i>	<i>b</i>	45.27	45.35	4.32	4.12
<i>p</i> - $\text{BrC}_6\text{H}_4$	91	251 dec.	628.12	<i>b</i>	<i>b</i>	42.07	41.74	4.01	3.93

<sup>a</sup> Mechrolab vapor pressure osmometer. <sup>b</sup> Insoluble.

solutions of sodium acetylacetonate and zinc acetate according to the procedure given by Dwyer and Sargeson.<sup>3</sup> The desired compound was obtained in poor yield; the major product was a compound of the empirical formula  $\text{Zn}(\text{C}_6\text{H}_7\text{O}_2)_2 \cdot \text{NaC}_2\text{H}_3\text{O}_2 \cdot \text{CH}_3\text{OH}$  and unknown structure.

It was not possible to carry out any further reactions with the sodium tris(acetylacetonato)zincate(II) thus prepared, due to its low solubility in alcohol and instability in the presence of water.

#### Experimental

**Anhydrous Bis(acetylacetonato)zinc(II).**—Reports about this product in the literature are rather inconsistent.<sup>2,4</sup> We prepared it in large runs *via* the unstable methanol adduct of bis(acetylacetonato)zinc(II).

Bis(acetylacetonato)zinc(II) hydrate (100 g.) was dissolved in 600 ml. of methanol. The flask containing the solution was packed in Dry Ice and stored with occasional shaking, until the temperature dropped to  $-50^\circ$ . The crystals formed were filtered rapidly through a precooled Büchner funnel and transferred to a round-bottom flask; extended contact with moist air was avoided. After 24 hr. drying under high vacuum 80 g. of anhydrous bis(acetylacetonato)zinc(II), m.p.  $127^\circ$ , was obtained. Unlike the monohydrate, this product dissolved readily in common organic solvents.

(4) D. P. Graddon and D. G. Weeden, *Australian J. Chem.*, **16**, 980 (1963).

**Preparation of Compounds  $\text{Zn}_2(\text{RCO}_2)(\text{C}_6\text{H}_7\text{O}_2)_3$ . General Procedure.**—Anhydrous bis(acetylacetonato)zinc(II) (10.5 g., 40 mmole) was dissolved in benzene. A solution of 20 mmole of the acid in benzene was added and the mixture allowed to stand overnight. The resulting crystals were filtered, washed with benzene and petroleum ether, and dried. Recrystallization did not significantly improve the elemental analyses.

When the acid is not sufficiently soluble in benzene, as in the case of *p*-chloro- and *p*-bromobenzoic acids, the components could be dissolved in hot xylene before being poured together.

**Preparation of  $\text{NaZn}(\text{C}_6\text{H}_7\text{O}_2)_3$  and  $\text{Zn}(\text{C}_6\text{H}_7\text{O}_2)_2 \cdot \text{NaC}_2\text{H}_3\text{O}_2 \cdot \text{CH}_3\text{OH}$ .**—Methanol solutions of sodium acetylacetonate (0.32 mmole) and zinc acetate (0.16 mmole) were combined. Sodium acetylacetonatozincate(II) (11.5 g., 0.03 mmole) precipitated immediately and was filtered and dried. The mother liquor, set aside in a freezer overnight, precipitated a crystalline colorless compound (decomposes above  $225^\circ$ ); the yield was 31.1 g. or 0.082 mole. The formula  $\text{Zn}(\text{C}_6\text{H}_7\text{O}_2)_2 \cdot \text{NaC}_2\text{H}_3\text{O}_2 \cdot \text{CH}_3\text{OH}$  was established by elemental analysis, by potentiometric titration of acetylacetone and acetic acid after aqueous phosphoric acid decomposition and steam distillation, and by v.p.c. detection of methanol in the decomposed aqueous solution.

*Anal.* Calcd. for  $\text{ZnNaC}_{13}\text{H}_{20}\text{O}_7$ : C, 41.34; H, 5.60; Zn, 17.31; Na, 6.09. Found: C, 41.05; H, 5.30; Zn, 17.17; Na, 5.69.

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